



Gamma Irradiation-Induced Preparation of Gum Arabic/ Poly (Vinyl Alcohol) Copolymer Hydrogels for Removal of Heavy Metal Ions from Wastewater

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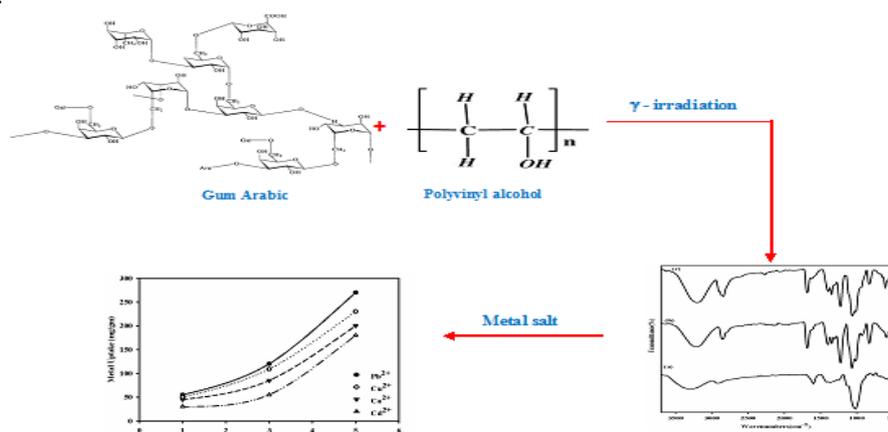
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Received 2nd Aug. 2019
Accepted 12th Dec. 2019

In this study, the copolymer hydrogel was prepared by copolymerization of gum arabic (GA), Poly (vinyl alcohol) (PVA) using gamma irradiation. The factors affecting the preparation conditions of (GA/PVA) copolymer hydrogels such as copolymer composition, copolymer concentration and irradiation dose were investigated. The swelling property of the prepared hydrogels was studied and the results showed that the swelling percent increased with increasing concentration of GA in feed solution and reached to the equilibrium state at 6 h. The obtained hydrogels were characterized using thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The morphology of the prepared hydrogels was examined by Scanning Electron Microscopy (SEM). The mechanical properties of copolymer hydrogel [tensile strength (TS), elongation at break (Eb) and compressive test (CS)] were measured using an Instron testing machine. The prepared hydrogels were investigated for the removal of Cu²⁺, Co²⁺, Pb²⁺ and Cd²⁺ ions from industrial wastewater. The parameters influencing the metal uptake, for example, pH, time, GA content and temperature were investigated. The adsorption of metal ions by hydrogel increases as follows Pb²⁺ > Cu²⁺ > Co²⁺ > Cd²⁺. The prepared copolymer hydrogel possessed a good affinity towards the adsorption of metal ions, which makes them acceptable for the treatment of industrial Wastewater from such metal ions.

Graphical Abstract



Keywords: Gum Arabic; PVA; Gamma Irradiation; Copolymerization; Heavy Metals.

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DOI: 10.21608/ajnsa.2019.15587.1246

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Introduction

The environmental pollution caused by human vigors accustoms dangerous trouble which has received rising interest all over the world. The rise of industrial vigors is responsible for an enormous quantity and number of pollutants released into the environment, among them heavy and toxic metals that collect in soil and finally transported to the human food chain, leading to health troubles [1]. Metals, for example, lead, cadmium, cobalt are very dangerous and highly toxic even in minor amounts. An expanding amount of substantial metals in our assets is at present a zone of more noteworthy concern, particularly since a huge number of industries are releasing their metal containing-effluents into freshwater with no satisfactory treatment [2]. There are many methods applied to eliminate these toxic metals as precipitation, neutralization, filtration, solvent extraction, ion-exchange resin and chemical chelating. These methods have many environmental, technical, economic, and health problems. However, adsorption [3], is an attractive method due to the lower cost of treatments and apparatus, ease of the process, easy handling, possibility of using various kinds of adsorbents, which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated wastewater [4]. Hydrogels can absorb water due to the existence of hydrophilic functional groups, for example, ($-\text{SO}_3\text{H}$), ($-\text{COOH}$), ($-\text{OH}$), ($-\text{CONH}_2$), ($-\text{CONH}-$) and others in the polymer backbone. The existence of these groups improves the capacity of water absorption for the hydrogels and furthermore goes about as effective anchors for active molecular species and metal ions. Thus, hydrogels can trap and absorb metal ions from Wastewater. Natural polysaccharides have an enormous domain of medical and industrial uses because of their safety, unique structure, biodegradability and distinguishing properties [5]. Gum arabic (GA) is a complex mixture of glycoproteins and polysaccharides consisting of arabinose and galactose. It is soluble in water, edible, and is used in different purposes such as paint production, as a stabilizer in the food industry, cosmetics, printing, glue, and different modern applications [6]. Poly (vinyl alcohol) is well known as a synthetic polymer that has an enormous application because of its remarkable physical and chemical characteristics as water solubility and nontoxicity. PVA is utilized

for various industrial applications due to its excellent water retention properties and also to enhance the mechanical properties of hydrogels because of its compatible structure and high hydrophilic properties [7]. Both GA and PVA have numerous ($-\text{OH}$) groups in their chemical structure, and the interactions between these groups is expected to form hydrogen-bonding. Hence mechanical and thermal properties could be enhanced. This hydrogel can be utilized to remove heavy metal ions from wastewater. Both GA and PVA are highly biocompatible, economical and of an environmentally friendly nature which makes them obvious choices for the synthesis of the hydrogel matrix.

The irradiation technique is used for polymer processing and modification. The irradiation of polymeric materials with ionizing radiation (e.g. gamma rays, X-rays, accelerated electrons and ion beams) leads to the formation of very reactive intermediates, free radicals, ions and excited states. These intermediates can follow several reaction paths that result in disproportion, arrangements and/or the formation of new bonds. The main interaction of ionizing radiation with polymers depends on its molecular weight and its ability induces crosslinking or scission which may result in the formation of a wide range of materials without introducing any chemical initiators and without dissolving the sample. Generally, crosslinking and chain scission occur simultaneously but one of them may dominate over the other. Therefore, the use of gamma radiation facility gives good results for preparation studies [8].

Survey of the literature reveals that gum arabic and poly (vinyl alcohol) hydrogel, have not been used for wastewater treatment. Consequently, the present investigation represents an attempt to develop good chelation and ion exchanger hydrogels based on gum arabic and poly (vinyl alcohol) using gamma irradiation techniques. The parameters affecting the preparation conditions; physical and mechanical properties were investigated for possible use of the prepared hydrogel in the removal of several heavy and toxic metals from the industrial wastewater.

Experimental

Materials

The materials used in this investigation included Gum Arabic (GA) (Qualikems, India). Poly (vinyl alcohol) (PVA) (Qualikems, New Delhi). Cupric sulfate pentahydrate ($\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$) (Qualikems,

India), Cadmium (II) chloride, 2.5-hydrate ($\text{Cd Cl}_2 \cdot 2.5\text{H}_2\text{O}$) (Reachim, Russia), Cobalt (II) chloride hexahydrate ($\text{Co Cl}_2 \cdot 6\text{H}_2\text{O}$) (GRG, Win Lab, South Korea), Lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) (Qualikems, India). Other chemicals and solvents are used without further purification.

Methods and Apparatus

a- Methods

Synthesis of Gum Arabic (GA), Poly (Vinyl Alcohol) (PVA) Copolymer Hydrogel by Gamma Irradiation

The (GA/PVA) copolymer hydrogel was synthesized using the gamma irradiation technique which took place by free radical mechanism. An aqueous solution of PVA was prepared by dissolving the known quantity of PVA in double-distilled water in a water bath with continuous stirring for 6 h and at 80°C . GA was dissolved in distilled water at room temperature and was added to the PVA solution to form (GA/PVA), mixture solutions with continuous stirring at 60°C for 3 h till homogeneous mixing was completed. The compositions of GA and PVA in the mixture solutions were (0/100), (20/80), (30/70), (40/60), (50:50) and (60:40) wt% and at different total copolymer concentration of (5, 10, 20 and 30 wt%). The synthesized solution was taken in glass test tubes and irradiated at (10, 20, 30, 40 and 50 kGy) using ^{60}Co gamma rays at the dose rate of 1.9 kGy/h. After copolymerization, the test tubes were broken, the hydrogel cylinders were eliminated and cut into plates of 2 mm thickness and 5 mm diameter. The samples were then washed with overabundance water to eliminate the unreacted materials and evaporated at room temperature to a constant weight.

Determination of Gelation Percentage

The prepared hydrogel was extracted with water at 60°C for 24 h to eliminate the soluble materials and then dried at room temperature to a constant weight. The gelation percent was then calculated as follows:

$$\text{Gelation (\%)} = [W_e/W_o] \times 100 \quad (1)$$

where W_e is the weight of extracted insoluble hydrogel and W_o is the initial weight of the dry hydrogel.

Swelling Behavior

The dried hydrogel was weighed (W_o) and flooded in double-distilled water for several intervals of

times at room temperature until the maximum swelling is reached. The overabundance of water on the outside of the hydrogel sample was eliminated with a filter paper and after that, the sample was weighed. The swollen hydrogel is then weighed (W_s) and the swelling percent was calculated from to the following equation:

$$\text{Swelling (\%)} = [(W_s - W_o) / W_o] \times 100 \quad (2)$$

Where W_o is the weight of dry hydrogel and W_s is the weight of the swelled hydrogel.

Adsorption of Heavy Metal Ion

A stock standard of Pb(II), Cd(II), Co(II) and Cu(II) ions solutions of 400 ppm was synthesized. The fodder solutions with various concentrations of metal ions were synthesized by dilution of the supplies solution. The steady weight of the prepared hydrogels is flooded in 10 ml of various metal ions concentrations and permitted to equate for various conditions. The hydrogel was eliminated from an aqueous solution at various time and the remaining concentrations of metal ions were specified by UV/VIS spectrometer and utilized for the calibration procedure. The adsorption amount (q_e) is determined as [9]:

$$q_e \text{ (mg/g)} = [(C_o - C_e) / W] \times V \quad (3)$$

where, C_o and C_e are the concentrations of metal ions in (mg/L) before and after the adsorption, respectively. Whereas V is the volume of solution (L), W is the weight of the dry hydrogel (g).

b- Apparatus

i. Fourier-Transform Infrared Spectroscopic Analysis (FTIR)

The infrared spectra of (GA/PVA) copolymer hydrogel were performed using an FT-IR spectrometer (Bruker, Unicomb, Germany in the range of $400\text{--}4000 \text{ cm}^{-1}$).

ii. Thermogravimetric Analysis (TGA)

The TGA thermograms of (GA/PVA) copolymer hydrogel were examined on a Shimadzu-50 instrument (Kyoto, Japan) under flow nitrogen (20 ml/min) from room temperature to 600°C and at a heating rate of $10^\circ\text{C}/\text{min}$.

iii. Measurement of Mechanical Properties

Mechanical properties of the (GA/PVA) copolymer hydrogel were measured at the laboratories of the National Research Center (NRC), Cairo.

a- Tensile Strength (TS) and Elongation at Break (Eb)

(GA/PVA) copolymer hydrogel was examined for tensile strength (TS) and elongation at break (Eb) with a ZWICK/ Roell/ Z010 testing machine (Germany) according to ASTM D638,05/2008.

b- Compression Measurements

Compression measurements were performed on the (GA/PVA) copolymer hydrogel using a compressive tester (ASTM D395-2017).

iv. UV-Vis Spectrophotometer

Metal ion concentrations were determined utilizing UV/VIS Spectrometer model UV-Analytic Jena AG, German, at room temperature with a scan range of 190–1100 nm depending on the type of metal.

Results and Discussion

1-Factors Affecting on Gelation Percent of (GA/PVA) Copolymer Hydrogel

The copolymerization of GA with PVA by gamma irradiation technique leads to the formation of crosslinked (GA/PVA) copolymer hydrogel which depends mainly on the copolymer composition, copolymer concentration as well as irradiation dose.

a- Effect of Copolymer Composition

The comonomer composition has a great effect on the gelation process. Normally, one of the two polymers may upgrade the gelation process of the other polymer or the other way around. The gelation percent of (GA/PVA) copolymer hydrogel, as a component of copolymer composition is shown in Fig. (1). It is clear that the gelation percent of the obtained (GA/PVA) copolymer hydrogel increases as the PVA content increases in the fodder solution because of the distinction of the difference in the diffusion coefficient of both polymers. The results are in good agreement with those reported by Mervat et al.,[10] who found that the increase of the polymer lead to an increase of the gelation percent in gum arabic hydrogels (GA with PVA). Also, increasing PVA content in the fodder solution leads to an increase of hydroxyl groups which increase the hydrogen bond interactions between the hydroxyl groups of PVA and the amide groups of GA in the polymeric matrix leading to a compact hydrogen-bonded structure [11]. It is also noted from the Figure that the highest gelation percentage was obtained at a copolymer

composition GA/PVA (0/100), because the PVA hydrogel can form dimmers through hydrogen bonding leading to rising in the cross-linking and the gelation percentage [12].

b- Effect of Copolymer Concentration

Figure (2) illustrates the relationship between the copolymer Fodder solution and gelation percentage of (GA/PVA) copolymer hydrogel. It is noted that the gelation percentage increases as the copolymer concentration increases in the fodder solution. In general, at high copolymer concentration, an enormous number of molecules are ready to interact with the free radical on the backbone of the polymer chain. Furthermore, the generation of a large number of developing chains would raise the probability of hydrogen abstraction through chain movement to offer increment to the substrate macroradicals. Thus, chain propagation was increased leading to an increase in the gelation percentage [13].

C-Effect of Irradiation Dose

It is recognized that degrees of crosslinking significantly rely upon the irradiation dose. The higher exposure dose implies longer irradiation time and thus expands the propagation stage of the copolymerization process leading to higher degrees of crosslinking. Gamma irradiation dose has two inverse impacts: (a) crosslinking impact where its increment prompted the increment in the thermal stability and (b) the degradation impact of higher dosages, which prompted a lowering in the thermal stability of the polymer. PVA is known to be a cross-linking polymer, while GA is a biodegradable polymer and degrades upon irradiation through the breakdown of the principal chains [14]. Figure (3) shows the effect of different irradiation doses on the gelation percentage of (GA: PVA) copolymer hydrogels in the range from 10 to 50 kGy. It is noted that the increase of irradiation dose from 10 to 40 kGy prompted the increment in the crosslinking which gives the polymer more thermal stability. As a consequence, the gelation percentage increases, which is a maximum at 40 kGy irradiation. Above this value the gelation percentage was decreased due to the intramolecular free radical recombination resorted to dominate over the intermolecular radical recombination, which would terminate the cross-linking and start to degrade the network [15].

Swelling Behavior

Effect of Time on the Swelling Percentage of (GA/PVA) Copolymer Hydrogel

The swelling of the hydrogel depends on the hydrophilicity of hydrogel chains, degree of cross-linking density, interactions of the network and surrounding liquid and the chemical composition of both polymers [13]. Figure (4) shows the swelling percent of (GA/PVA) copolymer hydrogel at different copolymer compositions. It is noted that the degree of swelling increases with time for different composition in distilled water, reaching equilibrium swelling at 6 h. The results show that the degree of swelling increases by increasing the GA content in (GA/PVA) copolymer hydrogel. This can be clarified on the premise that a high concentration of charged ionic groups (COO⁻) in the hydrogel increases the swelling because of charge repulsion and osmosis. i.e, the presence of increasingly ionic groups in the polymer chains that brings about incremented swelling due to the ionic groups are more robustly solvated than non-ionic groups in an aqueous medium [16]. Also, the hydrophilic nature of GA

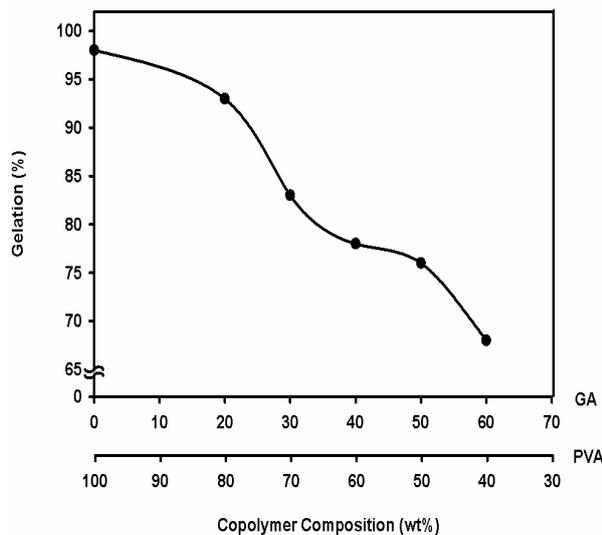


Fig. (1): Effect of copolymer composition on the gelation (%) of (GA/PVA) copolymer hydrogel; Copolymer concentration; 20 wt% and irradiation dose; 30 kGy

causes the formation of more hydrogen bonds between (–OH) of GA and (–H) in water molecules leading to an increase in the degree of swelling [17].

In addition, the existence of GA in the polymer solution decreases the probability of radical combination during irradiation, which decreases the cross-linking density of the gel. This prompts all the more free volumes in the polymer chain, and thus, more water can be absorbed. Furthermore, the swelling percent was reduced by increasing PVA content in the fodder solution. The results can be clarified by the fact that increasing content of PVA in the fodder solution will result in enhancing the cross-linking by intramolecular hydrogen bonding between the PVA chains in the hydrogel network structure [18, 19], which results in a tighter 3D-structure and decrease in the free volume, consequently lower swelling values, in comparison to the hydrogels, with lower cross-linking ratios [20, 21].

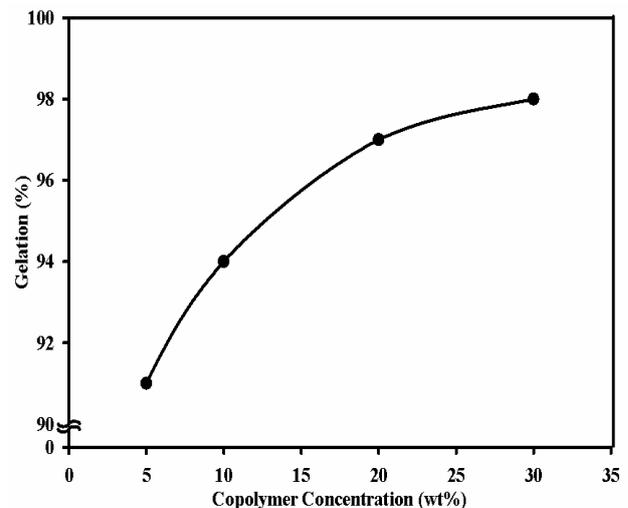


Fig. (2): Effect of copolymer concentration on the gelation (%) of (GA/PVA) copolymer hydrogel; Copolymer composition (20:80) (wt/wt) % and irradiation dose 30 kGy

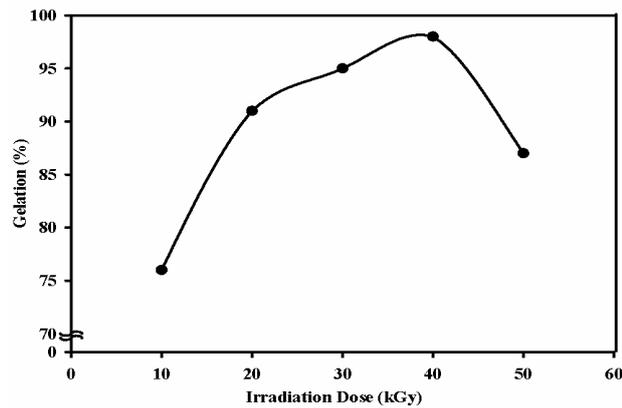


Fig. (3): Effect of irradiation dose on the gelation (%) of (GA/PVA) copolymer hydrogel; Copolymer composition (20:80) (wt/wt) % and copolymer concentration (20 wt%)

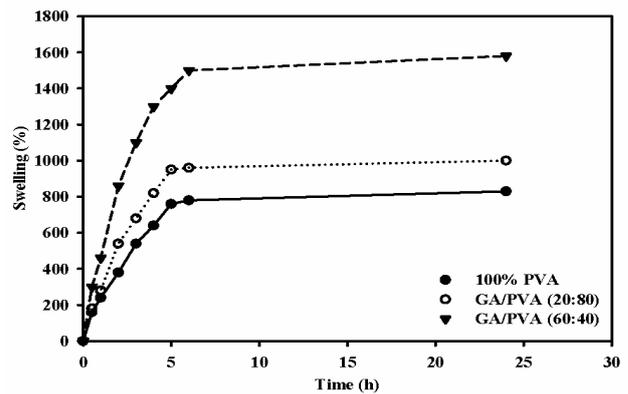


Fig. (4) Effect of soaking time on the swelling (%) of (GA/PVA) copolymer hydrogel; Copolymer concentration (20 wt%), irradiation dose (30 kGy) at room temperature (25°C)

Fourier-Transform Infrared Spectroscopic (FTIR) Analysis

FTIR is significant in considering the molecular structure. The width and intensity of the spectrum bands, just as the position of the bands, confirm the macromolecules on the molecular level. The FT-IR spectra of GA powder, blank PVA hydrogel and (GA/PVA) copolymer hydrogel of Copolymer composition (20:80) (wt/wt) % are shown in Fig. (5). It is obvious that, GA gives a typical broad band at 3200-3500 cm^{-1} corresponding to OH stretching and band appears at 2900 cm^{-1} corresponding to C-H stretching. Another absorption band appears at 1592 cm^{-1} corresponding to C=O stretching, and 1017 cm^{-1} corresponding to C-O stretching. The spectrum of blank PVA hydrogel fig.5(b) showed that, a broad band at 3200-3500 cm^{-1} corresponding to the OH stretching vibrations and the sharp band appears at 2927 cm^{-1} corresponding to asymmetric stretching of backbone aliphatic CH_2 of polymeric vinyl alcohol [19]. A new absorption band appears at 1720 cm^{-1} corresponding to C=O stretching of acetate groups of PVA and band appears at 1244 cm^{-1} corresponding to C-O stretching of PVA [19]. Another absorption sharp band at 1084 cm^{-1} corresponding to the symmetrical stretching C-O-C (an acetyl group) existing in the PVA chain and the bands in the range of 845-617 cm^{-1} due to the vinyl group. Figure 5 (c) shows the spectra of (GA/PVA) copolymer hydrogel which has both characteristic bands of GA and PVA. It is observed that the broad band between 3200-3500 cm^{-1} assigned to OH of the carboxylic group of GA is overlapping with the alcoholic OH of PVA. The

band at 1723 cm^{-1} , confirm that hydrogen bond interactions of PVA homopolymer are replaced by hydrogen bond interactions between GA and PVA. The C-O stretching vibration at 1084 cm^{-1} is slightly strengthened. This is due to the esterification reaction between the hydroxyl group in PVA and carboxylic groups in GA [9, 22, 23]. The FTIR spectrum of the copolymer hydrogel is much sharper and more intense than those of its components, GA and PVA. This is because of the crosslinking of PVA chains onto GA, the macromolecular chains form a free network wherein the grafted chains preferred pack up themselves to build a three-dimensional crystalline structure that shows well-defined sharp peaks [24].

Thermogravimetric Analysis

The thermal durability of hydrogels throughout its use is a very important tool for practical purposes, hence, the thermal gravimetric analysis was measured to examine experimentally the thermal stability of the synthesized copolymer hydrogels. The TGA for blank PVA hydrogel and (GA/PVA) copolymer hydrogel of Copolymer composition (20:80) (wt/wt) % and (60:40) (wt/wt) % were measured from room temperature up to 600°C. The TGA curves of blank PVA hydrogel and (GA/PVA) copolymer hydrogel reveal that there are three decomposition stages of weight loss, as represented in fig. (6). The first decomposition stage from ambient temperature to 100°C, is because of the dehydration process of the water in the hydrophilic polymers, which showed the thermal decomposition percentage 7%. The second decomposition stage, from 100 to 380°C, is

because of decomposition in branches of the hydrogel and the side groups with thermal decomposition percentage 51%. During the third stage, from 380 to 550°C, the weight loss is due to backbone degradation, which results in quick decomposition into volatile hydrocarbons and carbon dioxide [25].

The weight loss of blank PVA hydrogel and GA/PVA copolymer hydrogel increased with rising temperature, but GA/PVA copolymer hydrogel has undergone more weight loss than the blank PVA hydrogel. Thus, the thermal stability of the compositions of GA/PVA copolymer hydrogel is lower than that of blank PVA hydrogel, whereas the high residue content, up to 20 wt% at 600°C for blank PVA hydrogel. While the high residue content, up to 9, 1 wt%, at 600°C observed in thermogram for (GA/PVA) copolymer hydrogels of Copolymer composition (20:80) (wt/wt) % and (60:40) (wt/wt) %, respectively. This means that the thermal stability of prepared copolymer hydrogel improved with an increased amount of PVA in the Fodder solution [18].

Mechanical Properties

a- Tensile Strength (TS) and Elongation at Break (Eb)

Polymer materials, for example, hydrogels might be exposed to different sorts of stress during their utilization. Investigation of the mechanical properties is of essential significance for assessing the performance of the materials. There are numerous structural factors, which influence the mechanical conduct of such materials. In addition to the chemical composition, molecular weight, copolymerization, crosslinking, plasticization, branching and molecular orientation, their crystallinity, and fillers are structural factors, which influence the mechanical properties [26]. Two mechanical properties (TS) and (Eb) have been measured in the present work and results are shown in Fig. 8 (a, b). Figure (7a) shows the change in tensile strength (TS) with gelation (%) for (GA/PVA) copolymer hydrogel. It is obvious that the TS values increase with increasing gelation percentage. The notable increase in the tensile strength of the (GA/PVA) copolymer hydrogel indicated the existence of intermolecular interaction between PVA and GA molecules (due to the increased cross-linking density), i.e., the TS values increase with increasing the gelation (%) is due to the increased cross-linking of PVA [31].

Furthermore, the decrease in TS values by increasing GA content in the hydrogel is assigned to the degradation behavior of GA [27].

Flexibility and elasticity of the hydrogels are fundamental parameters that are always effectively considered during the utilization of the polymer. These two phenomena are identified with the elongation at break of the hydrogels. Figure (7b) shows the change in elongation at break (Eb) with gelation (%) for (GA/PVA) copolymer hydrogel. It is observed that Eb increased with increasing gelation percent, showing the same pattern of TS values [28]. It is clear that, Eb values were drastically increased for copolymer hydrogels due to incorporating PVA into the GA. It was attributed to the gradual increase in the concentration of highly flexible PVA into the copolymer hydrogels [29, 30]. Also, the crosslinking density increased with the increase in the gelation percentage, and this results in a higher Eb.

b- Compression Set Test

The compression set (CS) is a standard test for evaluating the elastic behavior of copolymers and was studied as a function of gelation (%) Table (1). The obtained results show that the hydrogels with a higher gelation percentage has relatively lower compression set value. As the PVA content incremented, the compression set is reduced. This is because as PVA loading increases the number of crosslinking density increases and crosslinking density suppress the flow of polymers chains and reduce compression set, i.e., as PVA loading increases the crosslinking density increases and the mobility of the polymers chains reduces, thus, induce stiffness in the filled compounds [30].

Application of the Prepared Copolymer Hydrogel in Wastewater Treatment

Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface [31]. Adsorption properties of adsorbent, which were prepared from (GA/PVA) copolymer hydrogel, were studied by varying heavy metal ions, contact time, PH of feed solution, GA content and temperature.

Effect of Time

The efficiency of copolymer hydrogel for the utilization in the purification of wastewater from heavy and toxic metal ions can be evaluated from

the required time to adsorb the maximum capacity of metal ions by chelation with the functional groups presented in the prepared copolymer hydrogel [32]. Figure (8) shows the metal ion uptake as a function of time for (GA/PVA) copolymer hydrogel. It is observed that the metal ion uptake increases with increasing time until the steady-state is reached within 6 h. The obtained data demonstrated that at the premier steps of the soaking time, the adsorption of metal ions was rapid, and then it becomes slower close to the equilibrium. This may be discussed in relation to the existence of an enormous number of unoccupied active sites in the premier stage which were prepared for adsorption, and then repulsion occurred between the adsorbate molecules on the adsorbent surface which hinder the adsorption procedure [33]. The results obtained show that (GA/PVA) copolymer hydrogel has a tendency towards metal ions according to the following order: $Pb^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+}$. These results can be explained by taking into consideration the diffusion coefficient of such metals through the pores of the copolymer hydrogel and stability of chelation of the metal ions with the copolymer hydrogel, which also depends on size of the hydrated ions, differences in electronegativity, free energy of hydration, and activity of metal ions [34]. The affinity of copolymer hydrogel towards such metal ions is due to the existence of a carboxylic acid group that is strong chemically bonded to metal ions. Moreover, GA in (GA/PVA) copolymer hydrogel acted as a chelating site for the previously selected transition metal ions [35].

Effect of the PH of Feed Solution

The initial pH of the solution plays a key role in the adsorption process since it impacts the aqueous metal ion speciation, the adsorbent surface charge, and the degree of ionization of the adsorbent during the adsorption process [36]. Figure (9) illustrates the variation of the adsorption capacity of (GA/PVA) copolymer hydrogel for Pb^{2+} , Cu^{2+} , Co^{2+} and Cd^{2+} ions in their particular individual solutions with the change in the pH of the medium. It is obvious that the amount of metal ions uptake of Pb(II), Cd(II), Co(II) and Cu(II) ions was increased by increasing the pH of the medium from (1 to 5) [37]. This is due to the fact that, at low pH values (acidic medium), the carboxylic groups of the hydrogel are protonated causing an electrostatic repulsion of cationic metal ions.

Along these lines, the competition between H and metal ions occurred, which prompts a reduction in the adsorption quantity. By increasing the pH, electrostatic repulsion is reduced by the unprotonation of carboxylic groups, prompting an increment of adsorption amount. At higher pH values (>5) the precipitation of metal ion $Pb(OH)_2$, $Cu(OH)_2$, $Co(OH)_2$ and $Cd(OH)_2$ has occurred and could not lead to an accurate interpretation of adsorption. Consequently, pH 5 is picked as the ideal pH for (GA/PVA) copolymer hydrogel for all metal ions [38].

Effect of GA Content

The number of functional groups existing in the prepared copolymer hydrogel plays an important role in determining the amount of metal ion uptake by copolymer hydrogel. Figure (10) shows the adsorption capacity of (GA/PVA) copolymer hydrogel of different GA contents (0, 20, 30, 60) wt% for Pb(II), Cd(II), Co(II) and Cu(II) ions. The (GA/PVA) copolymer hydrogel can interact particularly with divalent ions, e.g., Pb^{2+} , Cu^{2+} , Co^{2+} , and Cd^{2+} , owing to their chelate formation with electron-donating carboxyl groups [39] in a GA polymer which provides the capability of its (GA/PVA) copolymer hydrogel to form complexes with transition metal ions. The formation of the metal-chelated hydrogel is shown in Fig. (11). From the obtained data, it is obvious that the metal ion uptake increased with higher GA content in the polymeric matrix due to the fact that as the GA content increases the number of carboxylate groups increases and thus, the intermolecular repulsion forces increase resulting in the increases in the free spaces valid for swelling [40]. Also, GA-rich compositions possess high ions uptake that has a high swelling percent which increases the diffusion of the ions inside the hydrogels. In addition, at GA-poor copolymer fodder solution, the content of the crosslinked network structure is greater than that at GA-rich copolymer fodder solution, which hinders the diffusion of metal ions through such a network structure.

Effect of Temperature

The temperature of the medium is a significant factor in deciding the metal ions uptake by copolymer hydrogel. For investigating the effect of temperature, adsorption experiments were performed at 20, 25, 30, 35, 40 and 50°C. Figure (12) illustrates the effect of temperature on the

metal ions uptake (mg/g) for (GA/PVA) copolymer hydrogel. It very well noticed that the separation and sorption capacity increases with increasing temperature. This is because of the increment in the flexibility of the copolymer hydrogel chain and the kinetic energy of the metal ions, leading to higher diffusion of metal ions

through the bulk materials [41]. Diffusion is a function of the simplicity of the entrance of the metal ions through the polymer network. It was seen that the maximum metal ions uptake got at a temperature (50°C) at which the highest diffusion has occurred.

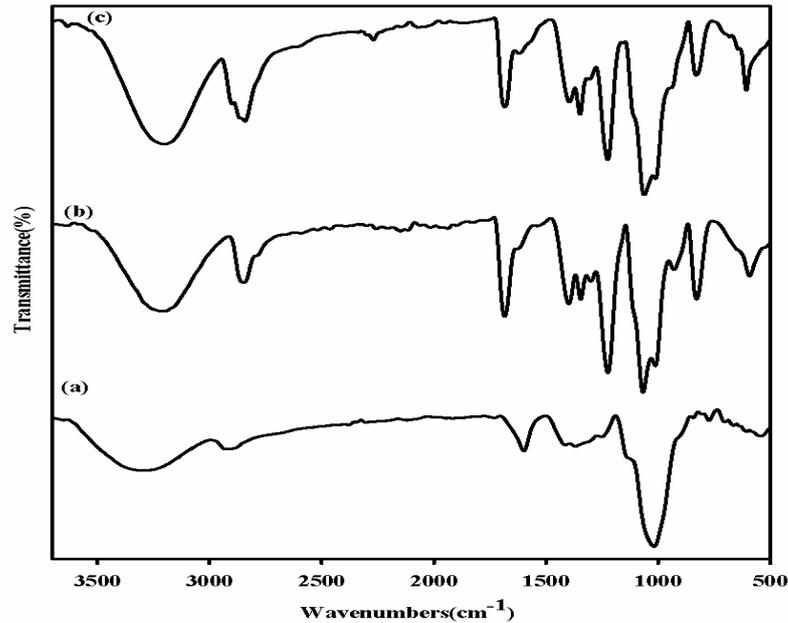


Fig. (5): FTIR spectra for (a) GA powder, (b) blank PVA hydrogel and (c) (GA/PVA) copolymer hydrogel of Copolymer composition (20:80) (wt/wt) %

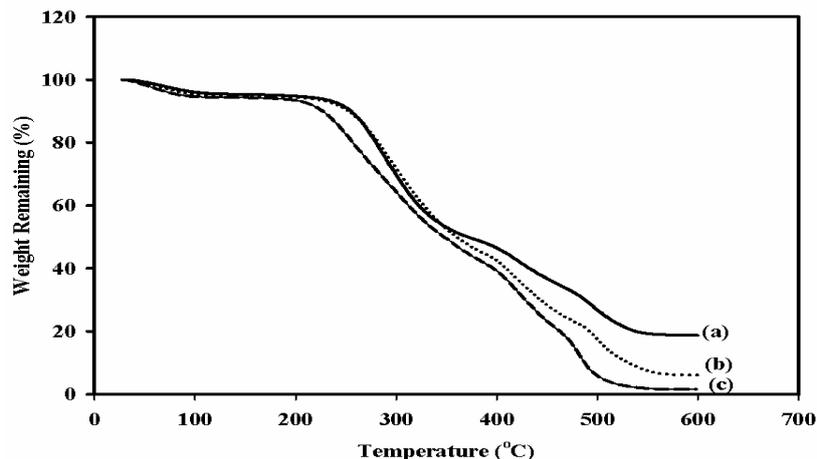


Fig. (6): TGA thermogram for (a) blank PVA hydrogel and (GA/PVA) copolymer hydrogel of copolymer composition (b) (20:80) and (c) (60:40) (wt/wt) %

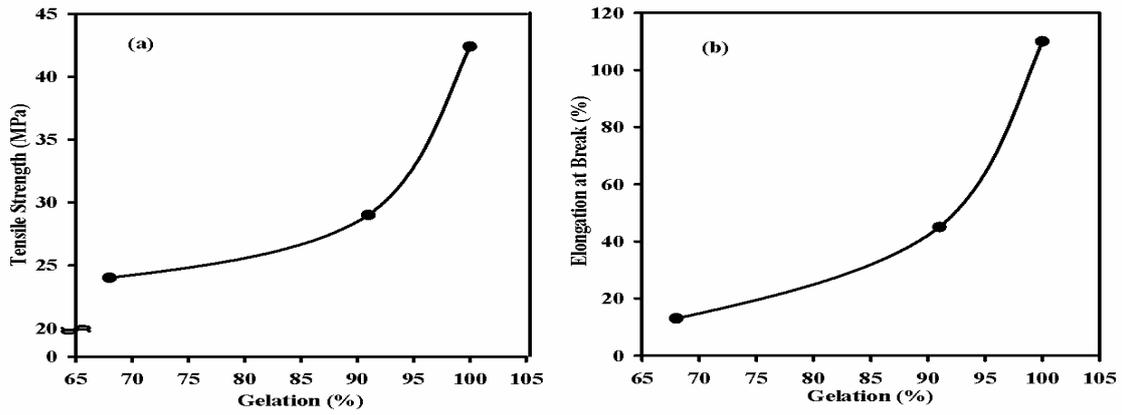


Fig. (7): The change in (a) tensile strength (TS) and (b) elongation at break (Eb) with gelation (%) for (GA/PVA) copolymer hydrogel

Table (1): The change in compression set (CS) with gelation (%) for (GA/PVA) copolymer hydrogel

Gelation (%) of (GA/PVA)	Compression set (%)
91%	3%
100%	2%

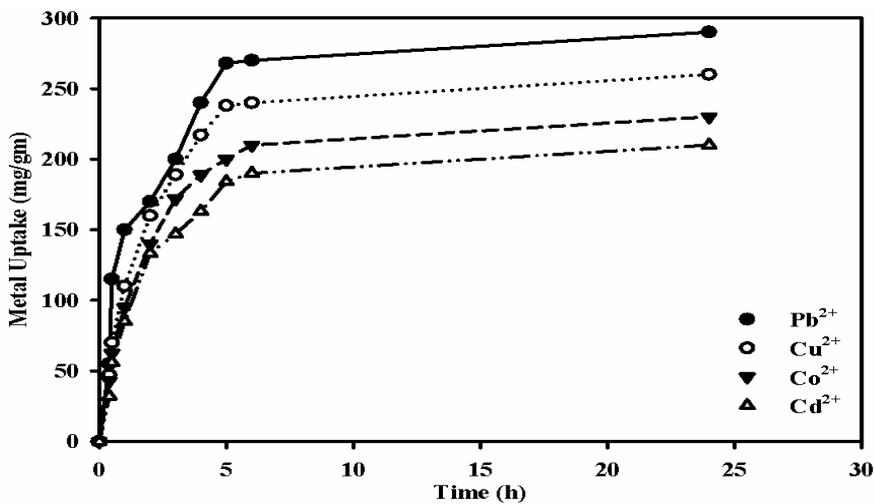


Fig. (8): Effect of soaking time on the metal uptake (mg/gm) by (GA/PVA) copolymer hydrogel; Gelation percent (91%), pH 5, initial feed concentration 400 ppm at room temperature (25°C)

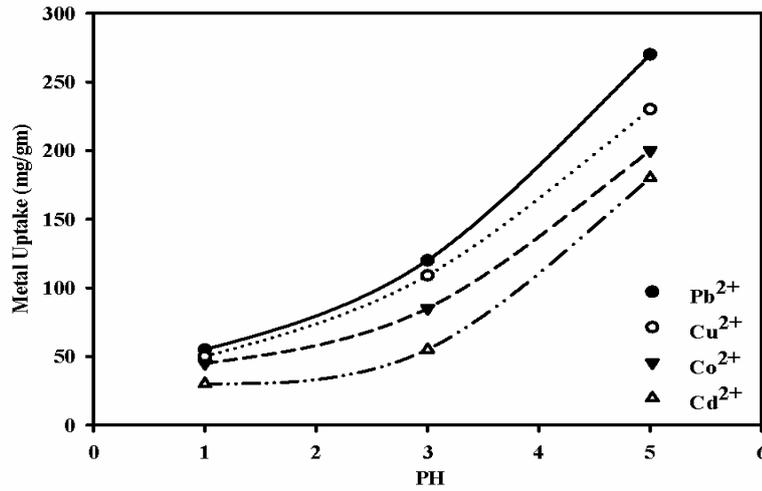


Fig. (9): Effect of pH on the metal uptake (mg/gm) by (GA/PVA) copolymer hydrogel; Gelation percentage (91%), time (6 h), initial feed concentration 400 ppm at room temperature (25°C)

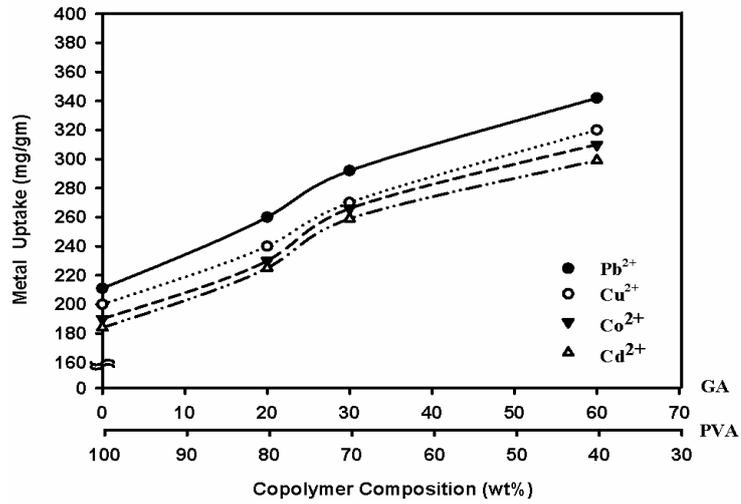


Fig. (10): Effect of GA content on the metal uptake (mg/gm) by (GA/PVA) copolymer hydrogel; pH 5, time (6 h), initial feed concentration 400 ppm at room temperature (25°C)

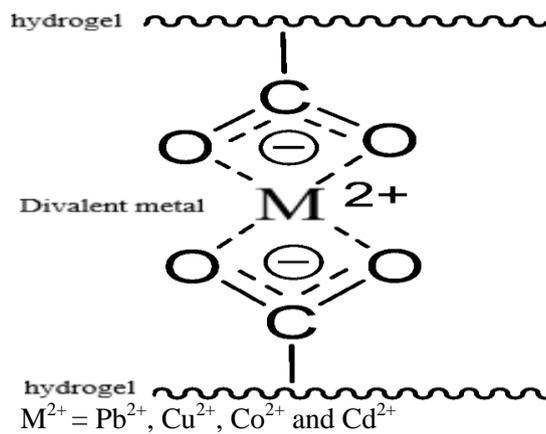


Fig. (11): Suggested structure of metal-chelated (GA/PVA) copolymer hydrogel

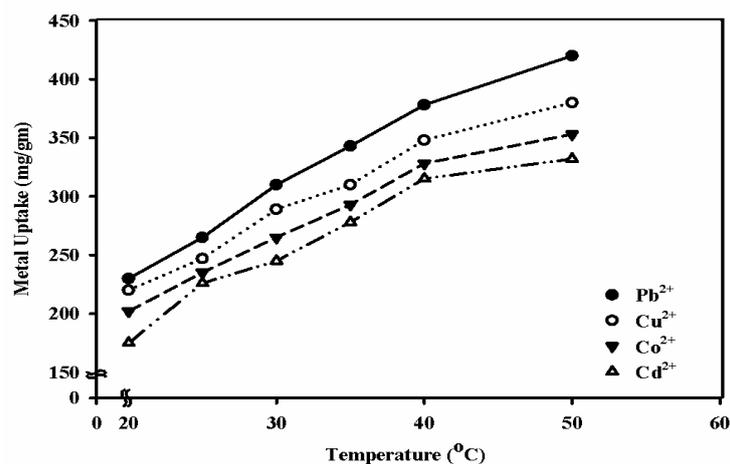


Fig. (12): Effect of temperature (°C) on metal uptake (mg/gm) by (GA/PVA) copolymer hydrogel; Gelation percent (91%), pH 5, time (6 h) and initial feed concentration 400 ppm.

Conclusion

In this study, (GA/PVA) copolymer hydrogel was successfully prepared by gamma irradiation. The prepared copolymer hydrogels were characterized using FTIR, TGA, SEM as well as the mechanical. The swelling percentage of copolymer hydrogel increased by increasing time, reaching equilibrium swelling at 6 h. The obtained data showed that the copolymer hydrogel has swelling properties reaching about 1600 (%). The prospect of using prepared copolymer hydrogels in the removal of some heavy metal ions was investigated. Factors affecting the adsorption process such as pH of the medium, contact time and temperature were studied. The results showed that the GA content is the major efficient factor for the affinity of the prepared copolymer hydrogels towards various metal ions from their aqueous solutions. The prepared copolymer hydrogels have a good affinity towards the adsorption of metal ions. This affinity was in the following order $Pb^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+}$, which makes them acceptable for the treatment of industrial wastewater to get rid of such metal ions.

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